THE FOURTEENTH MICROOPTICS CONFERENCE

MOC '08

Sept. 25 (Thu.)
Sept. 26 (Fr.)
Sept. 27 (Sat.)

TECHNICAL DIGEST

Organized by
Vrije Universiteit Brussel
Department of Applied Physics and Photonics

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Diamant Conference and Business Centre
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FUNCTIONAL POLYMER MATERIALS FOR OPTICAL APPLICATIONS

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Abstract: *One of the main limitations of the current generation of optical materials is the limited flexibility and stretch-ability. In the present paper, we therefore report on the development of a series of polymethacrylates in which the glass transition temperature was varied to obtain materials with enhanced flexibility. The monomers were selected in such a way that they are compatible with the materials often applied for waveguide production and optical fibre embedding.*
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1. Introduction

Polymer materials have found widespread applications in recent decades going from automotive over biomedical to optical applications. In the present work we aim to develop and characterise a series of functional polymer materials to be applied for optical applications: waveguide production and optical fibre embedding.

2. Materials and Methods

2.1 Material development

As a first generation polymer materials, we selected polymethacrylates. The chemical structure of the building blocks selected for the production of a series of (co)polymers is shown in the figure below.
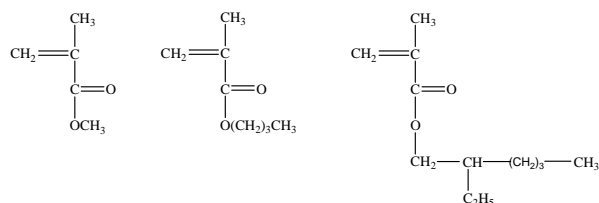

FIG. 1 Chemical structure of methyl methacrylate (MMA, left), butyl methacrylate (BuMA, middle) and 2-ethylhexyl methacrylate (EHMA, right).

Using the different monomers, homopolymers and copolymers with varying composition were synthesized by radical polymerisation in toluene using AIBN as radical initiator. After 24 hours at elevated temperature, the polymers were isolated by precipitation. Purification was performed by dialysis and/or reprecipitation.

2.2 Polymer analysis

The chemical structure of the (co)polymers was analysed by ^{1}H-NMR spectroscopy. Molecular weight analysis was performed using gel permeation chromatography. The thermal properties of the materials were analysed using DSC (differential scanning calorimetry) and TGA (thermogravimetric analysis) measurements on a TA instruments equipment DSC 2920 Modulated DSC and Hi-Res TGA 2950 Thermogravimetric Analyzer respectively

3. Results and Discussion

In the present work, we report on the development of a series of polymethacrylates containing MMA as comonomer to be applied for optical applications. The applications envisaged include materials for waveguide production and optical fibre embedding. The main drawback of the current generation optical materials is their limited flexibility and stretch-ability. The monomers (see figure 1) were selected in such a way that the flexibility of the materials obtained can be carefully fine-tuned by varying the selected comonomers and the comonomer ratios. An overview of the materials developed, their chemical composition and their corresponding glass transition temperature T_g are shown in the table below.

Table 1. Chemical composition as obtained by ^{1}H-NMR spectroscopy and thermal properties (T_g) of polymers developed.

	Composition (mol%)	T_g °C
TVG1	MMA/BuMA75/25	96
TVG2	MMA/BuMA42/48	66
TVG3	MMA/BuMA24/76	51
TVG4	MMA/EHMA79/21	51
TVG5	MMA/EHMA51/49	29
TVG6	MMA/EHMA21/79	-4

From the above data, it can be concluded that the flexibility of the materials can be significantly enhanced, as reflected by the decrease in T_g. The effect can be controlled by varying the chemical composition of the materials (e.g. BuMa versus EHMA). Similar effects on the T_g as observed using BuMA could be obtained using lower amounts of EHMA.

It has been reported before that vinyl polymers are often prone to monomer residues after isolation of the polymer. These residues can affect the optical properties of the materials developed. Therefore, an extensive purification method was established to remove any unreacted monomer. The procedure involves a combination of dialysis and repeated dissolution precipitation of the polymers. NMR spectroscopy revealed a successful purification procedure (as evidenced by the absence of monomeric vinyl peaks).

Using the materials developed, the applicability for optical applications was investigated for the production of waveguides. One of the materials which are often applied for optical applications is Truemode. In a first attempt to enhance the flexibility of these formulations after curing, varying amounts of the (co)polymers developed were used as flexibilising agent. Due to the compatibility with Truemode, the polymer materials could be combined with Truemode by dissolution. Thermal analysis revealed that the polymers developed remain stable at the processing temperatures of Truemode (± 200°C).

Preliminary tests indicate that the flexibility of Truemode can indeed be enhanced. The effect is dependent on the polymer type and its concentration. At present, this effect is being quantitatively studied using rheology, mechanical testing and thermal analysis on Truemode/polymethacrylates based materials.

To ensure a proper anchoring of the flexibilising polymers in the final cross-linked Truemode network, an alternative approach was also investigated in which polymethacrylates containing cross-linkable side-groups were developed. The chemical structure of the polymers developed is shown in the following figure.
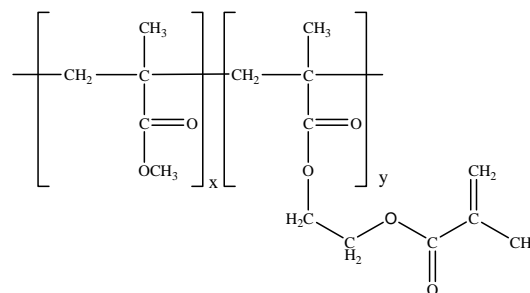

Fig 2. Chemical structure of X-linkable polymethacrylates.

At present, these materials are under evaluation for preparing formulations with Truemode. The results of this ongoing research will be presented during the meeting.

7. Conclusions

In the present work we have developed and characterized different methacrylate based homopolymers and copolymers that are applied for adjusting the flexibility of Truemode based formulations. The same polymers are currently also under evaluation for optical fibre embedding. For this purpose, a mould was already developed.

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Introduction

During the last decade, the development of smart flexible skins has attracted large attention for a variety of applications such as tactile sensors. [1]-[4] In the present work, we report on the development of flexible polymethacrylate based copolymers which will be applied for the embedding of optical fibres, waveguides and data processing units.

Materials and methods

The selection of the monomers, which are depicted in the figure below, was based on different crireria: biocompatibility, chemical resemblance with commercial materials (e.g. Truemode™) and fibre coating, ability to introduce functionalities and to change mechanical properties
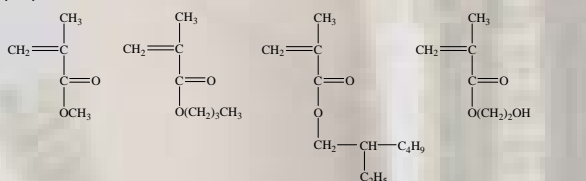

Fig. 1: Chemical structure of methyl methacrylate (MMA), butyl methacrylate (BuMA),

2-ethylhexyl methacrylate (EHMA) and 2-hydroxyethyl methacrylate (HEMA)

As depicted for the copolymerization of MMA and BuMA (see figure 2), the (co)polymerization reactions were carried out in toluene, in the presence of the radical initiator AIBN. After reaction, the (co)polymers were isolated by precipitation (10-fold excess of non-solvent) and filtration. Pure (co)polymers were obtained by repeated redissolution and precipitation in combination with dialysis.
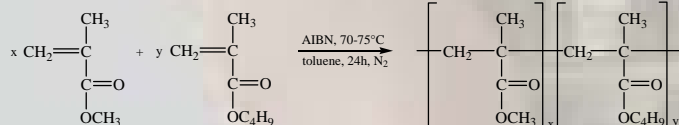

Fig. 2: Copolymerization reaction of MMA and BuMA

Structural characterisation and composition determination of the (co-)polymers was performed by means of ^{1}H-NMR in $CDCl_3$. Spectra were recorded on a Brüker 300 MHz spectrometer. Thermal properties of the materials were determined by means of DSC (differential scanning calorimetry) and TGA (thermogravimetric analysis) measurements on TA Instruments equipment DSC 2920 Modulated DSC and Hi-Res TGA 2950 Thermogravimetric Analyzer respectively.

Results and discussion

In order to be sure that the obtained copolymers had the desired composition, ^{1}H-NMR spectra of all the products were recorded. Table 1 shows that there was a good correlation between the theoretical and experimental composition of the developed copolymers.

Code	Theoretical composition (mol%)	Experimental composition (mol%)	T_g (°C)	T_d (°C)
TVG 1	MMA/BuMA 80/20	MMA/BuMA 75/25	96	228
TVG 2	MMA/BuMA 50/50	MMA/BuMA 52/48	66	231
TVG 3	MMA/BuMA 20/80	MMA/BuMA 24/76	51	---
TVG 4	MMA/EHMA 80/20	MMA/ EHMA 79/21	51	222
TVG 5	MMA/EHMA 50/50	MMA/ EHMA 51/49	29	230
TVG 6	MMA/EHMA 20/80	MMA/ EHMA 21/79	- 4	229

Table 1: Copolymer composition and thermal properties

One of the applications of the materials is the flexibilisation of Truemode™ waveguides by admixing copolymers in the commercial available Truemode™ formulation. A first indication about the flexibility of the copolymers developed can be given by the glass transition temperature (T_g) of the different materials, since the T_g of a material decreases with increasing flexibility. The results of the DSC measurements are shown in table 1. It can be observed that the glass transition temperature can be substantially lowered by partial replacement of MMA by BuMA. The effect is even more pronounced when EHMA is used.

To test the possible influence of the copolymers on the flexibility of a processed Truemode™ formulation, different mixtures with a varying copolymer concentration (10-100 mg/ml) were processed. Qualitative analysis confirmed an increased flexibility upon copolymer admixing. At present a quantitative mechanical analysis of the materials developed is ongoing.

Thermal stability of the materials was tested using TGA analysis. The temperatures at which 95% of the material was still intact, T_d, are depicted in table 1. The data show that the copolymers are compatible with the waveguide processing scheme, where maximum temperatures of 220-230°C are applied.
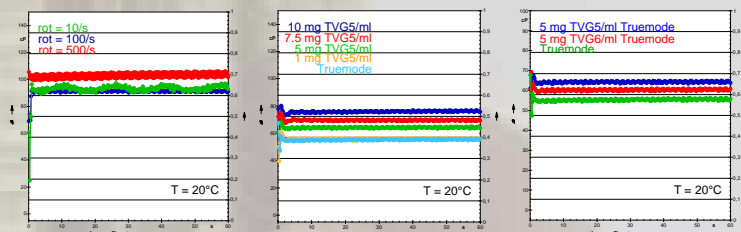

Fig. 3: Optimization of rotation speed (left), viscosity as a function of polymer concentration (middle), viscosity as a function of polymer type (right)

Rheological measurements prove that the added (co-)polymers have an influence on the Truemode™ material properties. An increase of viscosity is observed depending on the (co-)polymertype and –concentration.

In another track, the materials will be applied to embed optical fibres. To get an idea about the fibre embedding capacities of the (co-)polymers, an UV-transparent glass mould was fabricated by ultrasonic milling. Fibre alignment tools were produced by micromilling in stainless steel. The mould developed is depicted in the figure below.
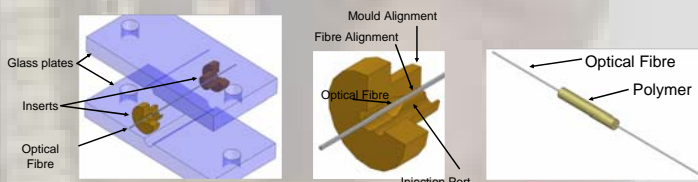

Fig. 4: UV transparent glass mould for fibre embedding purposes

The materials described so far, have one major drawback. Due to their chemical structure, they can not be chemically incorporated in the Truemode™ network. To create incorporable materials, HEMA based materials can be used, since the hydroxyl function can easily be modified into a cross-linkable group. To avoid uncontrolled cross-linking during the copolymerization of HEMA and other monomers (e.g. MMA), a Me_3Si-protected HEMA derivate was used. After the copolymerization reaction the protecting group was released by acid treatment with regeneration of the hydroxyl function, which can easily be transformed into a cross-linkable function. The coupling reaction of a HEMA based copolymer with methacrylic anhydride is depicted in the figure below.
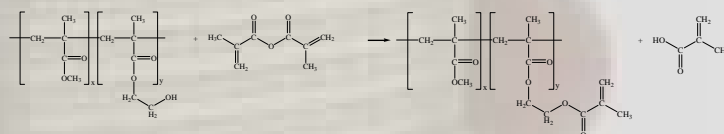

Fig. 5: Introduction of cross-linkable function using HEMA based copolymers

Outlook

In the near future, different properties of the Truemode/polymer combinations will be evaluated including mechanical properties and optical properties.

Conclusion

In the present work, we have developed series of methacrylate based copolymers to be applied for optical applications (fibre embedding & waveguide applications). For the different applications envisaged, flexible materials are a strong requirement. The preliminary results indicate that the polymers developed represent an ideal class of materials for fine-tuning the properties of existing materials as well as for embedding optical fibres.

Acknowledgement

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